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## ELECTRODE COMPOSITION, AND LITHIUMU SECONDARY BATTERY

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stability of such salts. More recently, novel lithium salt compounds such as those set forth in JP-T 2000-60834, too, have been proposed and practically used.

Another possible factor could be the electrochemical  
5 stability of solvents used for electrolyte solutions and the content of water in the solvents, and applications of additives and various solvents are now under consideration.

Thus, various methods have been used for high-temperature storage purposes. In consideration of the  
10 overall balance of battery properties, however, it is still difficult to improve high-temperature storage properties while keeping other battery properties intact. As an example, this is explained with reference to using  $\text{LiBF}_4$  as an electrolyte salt. This  $\text{LiBF}_4$  (hereinafter BF  
15 for short) is lower in conductivity than but superior in thermal stability to  $\text{LiPF}_6$  (PF for short). Accordingly, high-temperature storage properties, for instance, changes in the internal impedance of batteries as detected by the measurement of alternate currents upon storage become  
20 lower as compared when PF systems are used. However, low conductivity causes battery capacity to become lower than that of PF system batteries. In other words, when BF is used as an electrolyte salt, it is required to control the composition of an electrolyte solution solvent in view of  
25 such considerations and techniques incidental thereto are available as well. Still, the problem that the capacity is lower than that of PF systems remains unsolved.

For recent, more advanced mobile apparatus and instruments for which higher energy densities are needed,  
30 it is required to improve the properties of BF systems especially when batteries must have high capacities (when the amount of battery electrode active materials loaded is

increased), in particular keep capacity reductions at low levels.

More recently, batteries housed in flexible aluminum laminated films have been introduced so as to achieve ever  
5 higher capacities.

A problem with the aluminum laminated film is that as gases are produced from within a battery after the battery has been assembled, the battery swells. This problem may be surmountable by using  $\gamma$ -butyrolactone for  
10 its electrolyte solution as set forth typically in JP-A 2000-236868.

On the other hand, a problem with lithium secondary batteries is that their capacity becomes insufficient at low temperature. Some solutions to this problem are  
15 disclosed typically in JP-A's 06-290809 and 08-138738. However, these are chiefly directed to improvements in electrolyte solution compositions; it is still more difficult to improve the low-temperature properties on the premise that  $\gamma$ -butyrolactone should be used for prevention  
20 of battery swelling.

#### SUMMARY OF THE INVENTION

An object of the invention is to prevent the capacity of a battery from decrease when the aforesaid BF  
25 salts are used therefor.

Another object of the invention to provide a solution to the problem with the BF system especially when electrodes are designed to have high energy densities.

A more specific object of the invention is to  
30 provide a technique by which, when PVDF (polyvinylidene fluoride) is used as an electrode binder, a cyclic carbonate, especially EC (ethylene carbonate) is used as



above, wherein at least the poly(vinylidene fluoride) homopolymer, lactone and lithium fluoroborate-based salt are contained as solid electrolyte components.

(5) The lithium secondary battery according to (3) or (4) above, wherein a lithium-containing composite oxide comprising lithium cobalt oxide and a subordinate component element M, where M is a transition or typical metal element exclusive of Li and Co, in an amount of 0.001 to 2 at% relative to cobalt in the lithium cobalt oxide is contained as a cathode active substance, and 60 to 95% by volume of  $\gamma$ -butyrolactone is contained as an electrolyte solvent.

(6) The lithium secondary battery according to (5) above, wherein said subordinate component element is one or two or more of Ti, Nb, Sn and Mg.

(7) A lithium secondary battery, wherein:  
a cathode, an anode and an electrolyte are encased in a housing,  
a lithium-containing composite oxide comprising lithium cobalt oxide and a subordinate component element M, where M is a transition or typical metal element exclusive of Li and Co, in an amount of 0.001 to 2 at% relative to cobalt in the lithium cobalt oxide is contained as a cathode active substance,  
60 to 95% by volume of  $\gamma$ -butyrolactone is contained as an electrolyte solvent, and  
said housing has a thickness of 0.3 mm or smaller.

(8) The lithium secondary battery according to (7) above, wherein said subordinate component element is one or two or more of Ti, Nb, Sn and Mg.

WHAT IS ACHIEVED BY THE INVENTION





pressure and agitation to emulsion polymerization in the presence of a radical initiator, in substantially the absence of oxygen, and in the presence of an iodine or bromine compound, preferably a diiodine compound in an aqueous medium.

One advantage of the homopolymer obtained by the emulsion polymerization process is that it has very high purity or contains impurities in trace amounts of the order of ppb (parts by billion).

The homopolymer obtained by this emulsion polymerization process has a degree of crystallinity of 30% or higher, especially about 35 to 55%, and a molecular weight of preferably 50,000 or higher, more preferably 100,000 to 140,000.

Preferably for the electrode, a composition comprising an electrode active substance and a binder optionally with a conducting aid is used.

For an anode it is preferable to use an anode active substance such as a carbonaceous material, a lithium metal, a lithium alloy or an oxide material, and for a cathode it is preferable to use a cathode active substance such as an oxide or carbonaceous material capable of intercalating or deintercalating lithium ions. By using such electrodes, a lithium secondary battery having good enough properties can be obtained.

For the carbonaceous material used as the electrode active substance, for instance, an appropriate selection may be made from mesocarbon microbeads (MCMB), natural or man-made graphites, resin-fired carbonaceous materials, carbon blacks and carbon fibers, which are all used in powdery forms. Among others, preference is given to graphite having an average particle diameter of 1 to 30  $\mu\text{m}$ ,



especially 5 to 25  $\mu\text{m}$ . Too small average particle diameters would make charge/discharge cycle life short, and cause capacities to vary largely from battery to battery. Too large average particle diameters would lead to large capacity variations, resulting in an average capacity decrease. Why large capacity variations are caused with large average particle diameters could be due to fluctuations of contact of graphite with a collector or contacts of graphite particles with one another.

For the oxide capable of intercalating and deintercalating lithium ions, preference is given to lithium-containing composite oxides, for instance,  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$  and  $\text{LiV}_2\text{O}_4$ . Preferably, powders of these oxides should have an average particle diameter of the order of 1 to 40  $\mu\text{m}$ .

If required, conducting aids may be added to the electrode. For instance, graphites, carbon blacks, carbon fibers, and metals such as nickel, aluminum, copper and silver are used, although graphites and carbon blacks are particularly preferred.

Referring to electrode composition, the cathode should preferably have an active substance/conducting aid/binder ratio in the range of 80-94:2-8:2-18 by weight, and the anode should preferably have an active substance/conducting aid/binder ratio in the range of 70-97:0-25:3-10.

For electrode fabrication, the active substance and binder, optionally with the conductive aid, are first dispersed in a binder solution to prepare a coating solution.

Then, this coating solution is coated on a collector. Appropriately but not exclusively, the coating means

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## Lithium Secondary Battery

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The cathode, separator and anode are laminated together in this order, and then compressed together to obtain a battery body.

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salts such as  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiSO}_3\text{CF}_3$ ,  $\text{LiClO}_4$ , and  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  may be used. In the invention, however, lithium fluoroborates such as  $\text{LiBF}_4$  are used.

For the solvent for the electrolyte solution, any  
5 desired solvent may be used without restriction, provided that it should have favorable compatibility with electrolyte salts. Preferable for lithium batteries, etc., however, are polar organic solvents that do not decompose even at high operating voltages, for instance, carbonates  
10 such as ethylene carbonate (abbreviated as EC), propylene carbonate (PC), butylenes carbonate, dimethyl carbonate (DMC), diethyl carbonate and ethylmethyl carbonate, cyclic ethers such as tetrahydrofuran (THF) and 2-methyltetrahydrofuran, cyclic ethers such as 1,3-dioxolane,  
15 4-methyldioxolane, lactones such as  $\gamma$ -butyrolactone and sulforanes.

According to the invention, the solvent for the electrolyte solution should contain at least a lactone such as  $\gamma$ -butyrolactone. This lactone such as  $\gamma$ -  
20 butyrolactone should preferably be used in combination with the aforesaid solvents, especially the cyclic carbonate such as EC. The volume ratio between the cyclic carbonate and the lactone should preferably be in the range of 3/7 to 1/9, especially 1/3 to 3/17, as calculated  
25 on an ethylene carbonate-to- $\gamma$ -butyrolactone basis.

In the case where the electrolyte solution is made up of a solvent and an electrolyte salt, the concentration of the electrolyte salt should preferably be in the range of 0.3 to 5 mol/l. Usually at around 0.8 to 2.5 mol/l,  
30 the highest ion conductivity is found.

A solid electrolyte or separator sheet that forms the separator should preferably be formed of the aforesaid



µm, even more preferably 0.1 µm to 0.8 µm, and most preferably 0.1 µm to 0.6 µm. The microporous film should have a thickness of preferably 20 to 80 µm, and more preferably 25 to 45 µm.

- 5           The microporous film should preferably be formed of a material having a melting point of preferably 150°C or higher, especially 160 to 170°C and a heat of melting of preferably 30 J/g or greater, especially 40 to 60 J/g.

For the separator, still other gelled polymeric  
10 materials may also be used. For instance:

- (1) polyalkylene oxides such as polyethylene oxide and polypropylene oxide,
- (2) copolymers of ethylene oxide and acrylates,
- (3) copolymers of ethylene oxide and glycidyl ethers,
- 15 (4) copolymers of ethylene oxide, glycidyl ethers and allylglycidyl ethers,
- (5) polyacrylates,
- (6) polyacrylonitriles,
- (7) fluoropolymers such as polyvinylidene fluoride,
- 20 vinylidene fluoride-hexafluoropropylene copolymers, vinylidene fluoride-ethylene chloride trifluoride copolymers, vinylidene fluoride-hexafluoropropylene fluororubber, and vinylidene fluoride-tetrafluoroethylene-hexapropylene fluororubber.

- 25           The gelled polymer may be mixed with the electrolyte solution or coated on the separator. Moreover, if an initiator is used, the gelled polymer may be crosslinked together by means of ultraviolet rays, EB, heat or the like.

- 30           The solid electrolyte should preferably have a thickness of 5 to 100 µm, preferably 5 to 60 µm, and especially 10 to 40 µm. The solid electrolyte according

to the invention has so high strength that it can have a small thickness. The solid electrolyte according to the invention can be made thinner than a conventional gel electrolyte that cannot practically have a thickness of 60  
5  $\mu\text{m}$  or below, and than a separator (of usually 25  $\mu\text{m}$  in thickness) used with a solution type lithium ion battery. It is thus possible to achieve a thin yet large-area battery, i.e., a sheet form of battery that is one advantage of using the solid electrolyte.

10 Further, the separator may be formed of one or two or more of polyolefins such as polyethylene and polypropylene (when two or more are used, the film is of a multilayered structure), polyesters such as polyethylene terephthalate, thermoplastic fluororesins such as  
15 ethylene-tetrafluoroethylene copolymers, and celluloses. Furthermore, microporous films, woven fabrics and unwoven fabrics may be used, which have an air permeability of the order of 5 to 2,000 seconds/100 cc as measured according to the JIS-P8117 method and a thickness of the order of 5  
20 to 100  $\mu\text{m}$ .

A housing bag is formed of a laminated film in which heat-adhesive resin layers of polyolefinic resins such as polypropylene and polyethylene or heat-resistant polyester resin layers are laminated on both surfaces of an aluminum  
25 or other metal layer. The housing bag is formed with one side kept open by thermally bonding two laminated films together in such a way that heat-adhesive resin layers at the end faces of three sides thereof are thermally bonded together, thereby forming a first sealing portion.  
30 Alternatively, one laminated film is folded back so that the end faces of both sides are thermally bonded together to form a seal.

To ensure insulation between the metal foil forming the laminated film and a leading terminal, it is preferable to use a laminated film having a multilayered structure comprising, in order from its innermost side, a  
5 heat-adhesive resin layer/polyester resin layer/metal foil/polyester resin layer. By use of such a laminated film, it is possible to ensure a certain distance and so insulation between the leading terminal and the metal foil in the housing bag, because the high-melting polyester  
10 resin layer remains unfused during heat-bonding. Accordingly, the polyester resin layer in the laminated film should preferably have a thickness of the order of 5 to 100  $\mu\text{m}$ .

#### Second Embodiment

15 According to the second embodiment of the invention, there is provided a lithium secondary battery comprising a housing with a cathode, an anode and an electrolyte encased therein, wherein a cathode active substance contains a lithium-containing composite oxide comprising  
20 lithium cobalt oxide and a subordinate component element M, where M represents a transition or typical metal exclusive of Li and Co, in an amount of 0.001 to 2 at% relative to cobalt in the lithium cobalt oxide and a solvent for an electrolyte contains 60 to 95% by volume of  $\gamma$ -  
25 butyrolactone, said housing having a thickness of 0.3 mm or smaller.

With this embodiment, it is possible to provide a lithium secondary battery having satisfactory low-temperature properties with no outgassing even at high  
30 temperature. Even when a thin film form of housing is used, any swelling of the housing can be prevented.

In the lithium secondary battery according to the





substituted by two or more thereof. When two or more elements are used, they may be used in any desired combinations with the proviso that Co is substituted within the aforesaid total amount of substitution.

5           Usually, the anode comprises a carbonaceous material, a conducting aid and a binder. The conducting aid is the same as in the first embodiment.

          The carbonaceous material used herein, for instance, includes man-made graphite, natural graphite, pyrolytic  
10 carbon, cokes, fired resins, mesophase spheres and mesophase pitch.

          The binder used herein, for instance, include styrene-butadiene latex (SBR), carboxymethyl cellulose (CMC), polytetrafluoroethylene (PTFE), polyvinylidene  
15 fluoride (PVDF), ethylene-propylene-diene copolymers (EPDM), nitrile-butadiene rubber (NBR), vinylidene fluoride-hexafluoropropylene copolymers, vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene  
terpolymers, polytrifluoroethylene (PTrFE), vinylidene  
20 fluoride-trifluoroethylene copolymers, and vinylidene fluoride-tetrafluoroethylene copolymers.

          Electrode production is the same as in the aforesaid first embodiment.

          In the second embodiment, the non-aqueous  
25 electrolyte solution has a composition wherein an electrolyte is dissolved in a non-aqueous solvent comprising a mixed solvent that contains as a main component 60 to 95% by volume, preferably 70 to 90% by volume, especially 75 to 85% by volume of  $\gamma$ -butyrolactone  
30 (abbreviated as  $\gamma$ -BL) in a solvent component and further contains at least a solvent selected from a chain carbonate, a cyclic carbonate, a chain ester, etc. When

the composition ratio of  $\gamma$ -butyrolactone in the solvent  
departs from the range of 60 to 95% by volume, the  
formation of film on the surface of the carbonaceous  
material forming the electrode during initial charging  
5 becomes insufficient, resulting in a battery capacity  
decrease.

In the second embodiment, a sheet form of film  
having a thickness of 0.3 mm or smaller, especially 0.15  
mm or smaller is used for the battery housing, in which  
10 the cathode, anode and separator are located. It is here  
noted that the lower limit to the thickness of the housing  
is usually about 0.03 mm although the invention is not  
particularly limited thereto. This battery is tightly  
sealed in a vacuum-sealed state.

15 In the second embodiment, the housing is made up of  
a flexible film. By using the flexible film and  
evacuating the interior of the battery to a vacuum, the  
film is brought into close contact with the battery  
electrode. It is thus possible to fabricate a thin yet  
20 small-sized battery. While any limitation is not imposed  
on the structure of the film, it is preferable to use an  
aluminum laminated film with a resin layer inserted  
through it.

The housing formed of the flexible film makes for  
25 battery size reductions because the battery can be made  
thin. However, a problem with this housing is that its  
softness causes the battery to swell out even upon slight  
outgassing therefrom.

The cathode used in the second embodiment is  
30 superior in low-temperature properties to ordinary lithium  
cobalt oxides; however, the high activity of the electrode  
surface offers a problem that when, for instance, the

battery is stored in a full-charged state at high temperature, the cathode reacts with the electrolyte to produce gases.

For this reason, a small thin battery has the  
5 demerit of being unable to use any active substance of higher performance. As compared with dimethyl carbonate (DMC), methylethyl carbonate (MEC) and diethyl carbonate (DEC) often used with lithium secondary batteries usually encased in housing cans, the  $\gamma$ -butyrolactone used herein  
10 is less susceptible to oxidation and outgassing during high-temperature storage in a full-charged state. It is thus possible to use an active substance of higher performance even for batteries comprising housings formed of films that are thinner and softer than housing can  
15 materials that are relatively hard and less susceptible to deformation and, hence, fabricate small-sized yet high-performance batteries.

The second embodiment of the invention produces excellent effects even when applied by itself to a lithium  
20 secondary battery. It is understood, however, that this embodiment may be combined with the aforesaid first embodiment with synergistic effects which would enable more excellent lithium secondary batteries to be obtained.

## 25 EXAMPLES

Lithium cobalt oxide, etc. were used for the cathode active substance, and graphite-based materials for the anode active substance. Materials obtained by the carbonization of organic materials, too, may be used for  
30 the anode although their properties are different than those of the graphite materials.

### Example A-1

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Lithium cobalt oxide was used as the electrode active substance. For electrode preparation, various processes such as those mentioned above may be used. In this case, the following PVDF polymer was used as the binder.

PVDF Elf·Atochem Co., Ltd. (Atofina Co., Ltd.) Kynar 741

This PVDF was prepared by the emulsion polymerization process. With this binder, the electrode was prepared. In this example, a gelled solid electrolyte was used as the electrolyte. This gelled solid electrolyte was synthesized and prepared according to the process set forth in JP-A 11-276298.

More specifically,  $\text{LiCoO}_2$  was used as the cathode active substance, acetylene black as the conducting aid, and PVDF Kynar 741 as the binder.

These feeds were weighed in such a way as to give a ratio of  $\text{LiCoO}_2$ :acetylene black:PVDF = 83:6:11 by mass. Then, acetone was added in such a way as to give a ratio of acetone:PVDF = 9:1 by mass. These were mixed together at room temperature to obtain a cathode slurry.

On the other hand, mesocarbon microbeads (MCMB) were used as the anode active substance, and acetylene black as the conducting aid.

These feeds were weighed in such a way as to give a ratio of MCMB:acetylene black:PVDF = 85:3:12 by mass. Then, acetone was added in such a way as to give a ratio of acetone:PVDF = 9:1 by mass. These were mixed together at room temperature to obtain an anode slurry.

The thus obtained cathode and anode slurries were each coated by a doctor blade process on a PET film, and the acetone was then evaporated off at room temperature to obtain a sheet.

The following materials were used to prepare a microporous film for the electrolyte film, which was then used to obtain a solid electrolyte.

Twenty (20) parts by weight of polyvinylidene fluoride (Kynar 761 made by Elf·Atochem Co., Ltd.) were dissolved in a mixed solution comprising 40 parts by weight of dimethylacetamide and 40 parts by weight of dioxane, and the resulting solution was then cast by a doctor blade process on a glass sheet at a thickness of 200  $\mu\text{m}$ .

Immediately after the casting, the glass sheet was dipped in a solidifying bath comprising 80 parts by weight of dioxane and 20 parts by weight of water for 10 minutes for solidification, following which the glass sheet was washed in a water stream for 30 minutes, and then dried at 60°C for 1 hour, thereby obtaining a microporous film having a thickness of 50  $\mu\text{m}$  and comprising a poly(vinylidene fluoride) homopolymer.

The thus obtained microporous film was found to have a porosity of 70% and a pore diameter of 0.2  $\mu\text{m}$ .

To give adhesion to the surface of the aforesaid microporous film, it is acceptable to deposit a polyolefinic material thereon by spraying or the like.

The solid electrolyte, cathode and anode were each cut to given size, and the resultant sheets were heat-laminated together at 130 to 160°C. Then, an aluminum grid with a conductive adhesive coated ahead thereon as a collector was heat-laminated on the cathode while a copper grid with a conductive adhesive coated ahead thereof as a collector was heat-laminated on the anode.

Subsequently, the battery assembly was impregnated with an electrolyte comprising 1M  $\text{LiBF}_4/\text{EC} + \gamma$ -

butyrolactone (EC:γ-butyrolactone = 2:8 by volume), and then sealed in an aluminum laminated pack to obtain a lithium secondary battery.

The thus assembled battery was measured for its post-charging capacity on the basis of the capacity of a previously fabricated PF system battery. This PF system battery was the same as disclosed with reference to the BF system battery in Example A-1 except the following point.

Electrolyte solution composition EC:DEC = 3:7

#### 10 Comparative Example A-1

In this comparative example, PVDF KF1000 was used for the binder. This was prepared by suspension polymerization. Otherwise, Example A-1 was followed. By the same process as in Example A-1, a battery was fabricated and measured for its capacity.

#### Example A-2

A battery was obtained in the same manner as in Example A-1 with the exception that the electrolyte solution composition was changed to EC:γ-butyrolactone = 7:2.

#### Comparative Example A-2

In this comparative example, a battery was obtained in the same manner as in Example A-1 with the exception that the electrolyte solution composition was changed to EC:DEC = 3:7.

The results of these examples were summarized in Table 1. The rate of capacity decreases shown in Table 1 provides an indication of to what degree the initial capacity decreases from the reference capacity of the PF system battery.

ALL INFORMATION CONTAINED HEREIN IS UNCLASSIFIED

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Example B-1

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charging and discharging with the exception that the cathode active substance was changed to  $\text{LiCo}_{0.999}\text{Sn}_{0.001}\text{O}_2$ . After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

Example B-4

A battery was assembled as in Example B-1 for charging and discharging with the exception that the cathode active substance was changed to  $\text{LiCo}_{0.999}\text{Mg}_{0.001}\text{O}_2$ . After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

Example B-5

A battery was assembled as in Example B-1 for charging and discharging with the exception that the cathode active substance was changed to  $\text{LiCo}_{0.99999}\text{Nb}_{0.00001}\text{O}_2$ . After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

Example B-6

A battery was assembled as in Example B-1 for charging and discharging with the exception that the cathode active substance was changed to  $\text{LiCo}_{0.9999}\text{Nb}_{0.0001}\text{O}_2$ . After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

Example B-7

A battery was assembled as in Example B-1 for charging and discharging with the exception that the cathode active substance was changed to  $\text{LiCo}_{0.99}\text{Nb}_{0.01}\text{O}_2$ . After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery

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### Comparative Example B-2

A battery was assembled as in Example B-1 for charging and discharging with the exception that the cathode active substance was changed to  $\text{LiCo}_{0.9}\text{Nb}_{0.1}\text{O}_2$ . After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

### Comparative Example B-3

A battery was assembled as in Example B-1 for charging and discharging with the exception that the electrolyte solution composition was changed to ethylene carbonate (EC) and  $\gamma$ -butyrolactone at a ratio of 5:5 by volume. After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

15 Comparative Example B-4

A battery was assembled as in Example B-1 for charging and discharging with the exception that the electrolyte solution composition was changed to  $\gamma$ -butyrolactone = 100 by volume. After placed in a full-  
20 charged state, the battery was loaded in an oven to measure changes in the battery thickness.

### Comparative Example B-5

A battery was assembled as in Example B-1 for charging and discharging with the exception that the electrolyte solution composition was changed to ethylene carbonate (EC) and diethyl carbonate (DEC) at a ratio of 2:8 by volume. After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

30 Comparative Example B-6

A battery was assembled as in Example B-1 for charging and discharging with the exception that the

electrolyte solution composition was changed to ethylene carbonate (EC) and methylethyl carbonate (MEC) at a ratio of 2:8 by volume. After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

### Comparative Example B-7

A battery was assembled as in Example B-1 for charging and discharging with the exception that the cathode active substance was changed to  $\text{LiCo}_{0.999}\text{Ti}_{0.001}\text{O}_2$  and the electrolyte solution composition was changed to ethylene carbonate (EC) and methylethyl carbonate (MEC) at a ratio of 2:8 by volume. After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

15 Comparative Example B-8

A battery was assembled as in Example B-1 for charging and discharging with the exception that the cathode active substance was changed to  $\text{LiCo}_{0.999}\text{Sn}_{0.001}\text{O}_2$  and the electrolyte solution composition was changed to ethylene carbonate (EC) and methylethyl carbonate (MEC) at a ratio of 2:8 by volume. After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness.

### Comparative Example B-9

25           A battery was assembled as in Example B-1 for  
charging and discharging with the exception that the  
cathode active substance was changed to  $\text{LiCo}_{0.999}\text{Mg}_{0.001}\text{O}_2$  and  
the electrolyte solution composition was changed to  
ethylene carbonate (EC) and methylethyl carbonate (MEC) at  
30   a ratio of 2:8 by volume. After placed in a full-charged  
state, the battery was loaded in an oven to measure  
changes in the battery thickness.



Table 2

Sample	Substituent Element/at (%)	Solvent /volume	1C Capacity (mAh)	Specific Capacity -20°C (%)	Swelling During Storage at 90°C	
					0	after 30 min. after 4 hr.
Example 1	Nb/0.1	EC: $\gamma$ BL/2:8	570	20	4.23	4.31
Example 2	Ti/0.1	EC: $\gamma$ BL/2:8	567	18	4.25	4.30
Example 3	Sn/0.1	EC: $\gamma$ BL/2:8	566	15	4.23	4.32
Example 4	Mg/0.1	EC: $\gamma$ BL/2:8	564	13	4.22	4.33
Example 5	Nb/0.001	EC: $\gamma$ BL/2:8	571	12	4.20	4.23
Example 6	Nb/0.01	EC: $\gamma$ BL/2:8	571	16	4.20	4.25
Example 7	Nb/1	EC: $\gamma$ BL/2:8	566	16	4.21	4.26
Example 8	Nb/2	EC: $\gamma$ BL/2:8	562	14	4.23	4.29
Example 9	Nb/0.1	EC: $\gamma$ BL/4:6	561	15	4.24	4.28
Example 10	Nb/0.1	EC: $\gamma$ BL/5:95	565	13	4.23	4.30
Comp. Ex. 1	Nb/0.0001*	EC: $\gamma$ BL/2:8	572	8 <sup>+</sup>	4.21	4.26
Comp. Ex. 2	Nb/10*	EC: $\gamma$ BL/2:8	498 <sup>x</sup>	18	4.23	4.34
Comp. Ex. 3	Nb/0.1	EC: $\gamma$ BL/5:5*	526 <sup>x</sup>	17	4.25	4.30
Comp. Ex. 4	Nb/0.1	$\gamma$ BL/100*	512 <sup>x</sup>	19	4.22	4.28
Comp. Ex. 5	Nb/0.1	EC: DEC/2:8*	572	13	4.23	4.55 <sup>++</sup>
Comp. Ex. 6	Nb/0.1	EC: MEC/2:8*	574	27	4.22	5.16 <sup>++</sup>
Comp. Ex. 7	Ti/0.1	EC: MEC/2:8*	572	25	4.20	4.94 <sup>++</sup>
Comp. Ex. 8	Sn/0.1	EC: MEC/2:8*	571	20	4.24	4.88 <sup>++</sup>
Comp. Ex. 9	Mg/0.1	EC: MEC/2:8*	571	21	4.23	4.98 <sup>++</sup>
Comp. Ex. 10	—*	EC: $\gamma$ BL/2:8	566	7 <sup>+</sup>	4.23	4.28

<sup>\*</sup>) deviations from the inventive range<sup>†</sup>) deviations from the allowable range for -20°C specific capacity

deviations from the allowable range for swelling during storage

<sup>x</sup>) deviations from the allowable range for 1C capacity



In Example B-1, the binder used in Example A-1 and obtained by the emulsion polymerization process was used for the cathode. Otherwise, a battery was assembled as in Example B-1 for charging and discharging. After placed in a full-charged state, the battery was loaded in an oven to measure changes in the battery thickness. By the same method as in Example A-1, the capacity of the battery was measured. As in Example B-1, no battery swelling was found, and the rate of capacity decreases was on the same low level as in Example A-1.

From the foregoing results, it has been found that by using the binder of Example A-1 and the cathode active substance of Example B-1, effects equivalent to those of both Examples A-1 and B-1 are obtained.

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## ADVANTAGES OF THE INVENTION

As detailed above, according to the first embodiment of the invention, it is possible to provide an electrode composition which can reduce capacity decreases experienced when BF salts are used, and a lithium secondary battery.

According to the second embodiment of the invention,  
it is possible to provide a lithium secondary battery  
having high discharge capacity even at low temperature and  
unlikely to swell even during storage.